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(54) Title: METHODS AND COMPOSITIONS FOR SEALING AN EXPANDABLE TUBULAR IN A WELLBORE

(57) Abstract: Methods and compositions are provided for sealing an expandable tubular in a wellbore wherein the methods basically comprise placing the expandable tubular in the wellbore, placing a resilient sealing composition into the wellbore, expanding the expandable tubular and allowing the sealing composition to set in the wellbore.

Methods and Compositions for Sealing An Expandable Tubular In A Wellbore

Background

The present embodiment relates generally to a composition for sealing a subterranean zone penetrated by a wellbore and, more particularly, to methods and compositions for sealing an expandable tubular such as a pipe, pipe string, casing, liner or the like in a wellbore.

In the drilling and completion of an oil or gas well, a composition is often introduced in the wellbore for cementing casing or pipe strings. In this process, known as "primary cementing," a composition is pumped into the annular space between the walls of the wellbore and the pipe string. The composition sets in the annular space, supporting and positioning the pipe string, and forming a substantially impermeable barrier which divides the wellbore into subterranean zones. After primary cementing, the undesirable migration of fluids between zones is prevented. Likewise, compositions are often subsequently introduced into a subterranean zone for remedial operations to recover circulation or to plug the wellbore. Most remedial operations comprise introducing a composition into the wellbore to reestablish a seal between the zones.

Previously, a variety of cement compositions have been used for cementing. However, cement is undesirable for use with expandable casing. After the expandable casing is placed down hole, a mandrel is run through the casing to expand the casing, and expansions up to twenty five percent are possible. As cement is incompressible, expansion of the casing can lead to crushing of the cement, and consequent loss of effectiveness regarding the zones. Therefore, a resilient sealing composition with comparable strength to cement, but greater elasticity and compressibility is required for cementing expandable casing.

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Description

A sealing composition according to the present embodiment basically comprises a polymer and metal containing compound. A particularly preferred sealing composition comprises a mixture of latex, dithio carbamate, zinc oxide, and sulfur, for sealing a subterranean zone penetrated by a wellbore. The sulfur containing component vulcanizes the latex to form a solid mass which seals the zone. Preferred polymeric sealing compositions of the present invention are resilient with comparable strength to cement but have greater elasticity and compressibility for use in cementing expandable casing.

In a first embodiment, the composition comprises a mixture of latex, dithio carbamate, zinc oxide, and sulfur. Preferably, the amount of latex is maintained at a 41-90 percent ratio by weight of the composition. The dithio carbamate is preferably present in an amount that is 0.1-2 percent of the latex by weight. The zinc oxide is preferably present in an amount that is 2-5 percent of the latex by weight. The sulfur is preferably present in an amount that is 1-4 percent of the latex by weight.

The composition may further comprise stearic acid. The stearic acid is preferably present in an amount that is 0.1-2 percent of the latex by weight.

The composition may further comprise a weighting agent. The weighting agent is preferably present in an amount that is 0.1-150 percent of the latex by weight.

The composition may further comprise acetylenic alcohol for defoaming, such as is available from Halliburton Energy Services of Duncan, Okla., under the trademark "D-AIR3TM." The acetylenic alcohol is preferably present in an amount that is 0.001-0.2 percent of the latex by weight.

In a second embodiment, the sealing composition comprises a mixture of latex, dithio carbamate, zinc oxide, sulfur, and a foaming agent, wherein the mixture is foamed using a gas, such as nitrogen or air, which is generally present in the range of from about 0% to about 40% by volume of the sealing composition. Preferably, the amount of latex is maintained at a 41-90 percent ratio by weight of the composition. The dithio carbamate is preferably present in an amount that is 0.1-2 percent of the

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latex by weight. The zinc oxide is preferably present in an amount that is 2-5 percent of the latex by weight. The sulfur is preferably present in an amount that is 1-4 percent of the latex by weight. The foaming agent is preferably present in an amount that is 2-4 percent of the latex by weight.

The composition may further comprise stearic acid. The stearic acid is preferably present in an amount that is 0.1-2 percent of the latex by weight.

The composition may further comprise a weighting agent. The weighting agent is preferably present in an amount that is 0.1-150 percent of the latex by weight.

As will be understood by those skilled in the art, polymeric sealing compositions of the present invention may include any of a variety of well known polymers including, but not limited to, copolymers, terpolymers and interpolymers. Latex is preferably used for either embodiment and may be any of a variety of well known rubber materials commercially available which contain unsaturation in the backbone of the polymer. These include natural rubber (cis-1,4-polyisoprene), modified types thereof, synthetic polymers, and blends of the foregoing. The synthetic polymers include styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber. Additional polymers suitable for either embodiment include an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer. Preferably, the halogenated derivatives are halogenated with chlorine or bromine.

The metal containing compounds of the present invention may comprise zinc, tin, iron, selenium magnesium, chromium, nickel, or cadmium. Further, the compounds may be in the form of an oxide, carboxylic acid salt, a complex with a

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dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

For either embodiment, the composition preferably includes a latex comprising a styrene/butadiene copolymer latex emulsion prepared by emulsion polymerization. The weight ratio of styrene to butadiene in the latex can range from 10:90 to 90:10. The emulsion is a colloidal dispersion of the copolymer. The colloidal dispersion includes water from about 40-70% by weight of the emulsion. In addition to the dispersed copolymer, the latex often includes small quantities of an emulsifier, polymerization catalysts, chain modifying agents and the like. Also, styrene/butadiene latexes are often commercially produced as terpolymer latexes which include up to about 3% by weight of a third monomer to assist in stabilizing the latex emulsions. Non-ionic groups which exhibit steric effects and which contain long ethoxylate or hydrocarbon tails can also be present.

Most preferably for either embodiments, the composition includes a latex with a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion, available from Halliburton Energy Services of Duncan, Okla., under the trademark "LATEX 2000TM."

The weighting agent for either embodiment may be silica flour, such as is available from Halliburton Energy Services of Duncan, Okla., under the trademark "SSA-1TM." Alternatively, the weighting agent may be manganese oxide weighting additive, available from Halliburton Energy Services of Duncan, Okla., under the trademark "MICROMAXTM." Alternatively, the weighting agent may be crystalline silica with an average particle size of 10 microns, available from Halliburton Energy Services of Duncan, Okla., under the trademark "MICROSANDTM."

Dithio carbamate for either embodiment is available from Halliburton Energy Services of Duncan, under the trademark "FLEXCEM COMPONENT LTM."

The foaming agent for the second embodiment may be an ethoxylated alcohol ether sulfate surfactant, which is available from Halliburton Energy Services of Duncan, under the trademark "ZONE SEAL 2000TM." The ZONE SEAL 2000 surfactant is the subject of U.S. Patent No. 6,063,738, the entire disclosure of which is

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incorporated herein as if reproduced in its entirety. Alternatively, the foaming agent may be an amidopropylbetaine surfactant, which is available from Halliburton Energy Services of Duncan, under the trademark "HC-2TM." The HC-2TM surfactant is discussed in U.S. Patent No. 5,588,489, the entire disclosure of which is incorporated herein as if reproduced in its entirety.

The following examples are illustrative of the methods and compositions discussed above.

EXAMPLE 1

To test curing properties of the first embodiment, 450 grams of LATEX 2000TM latex, and components in the amounts listed in TABLE 1 were added to form three batches. Each of the batches was mixed in a Waring blender. The batches were poured into receptacles and incubated at the temperatures listed.

TABLE 1

Component	Batch 1	Batch 2	Batch 3
FLEXCEM COMPONENT L TM dithio carbamate	5.6g	5.6g	4.5g
Zinc Oxide	9g	9g	22.5g
Sulfur	9g	9g	13.5g
Stearic acid	--	9g	4.5g
D-AIR3 TM acetylenic alcohol	14.6g	14.6g	3g
SSA-1 TM silica flour	600g	600g	--
Comments	No Set; 48hr at 80°F	Set; 48hr at 150°F	Set; 5.5hr at 150°F

TABLE 1 shows that the second and third batches set.

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EXAMPLE 2

To test curing properties of the first embodiment with a different weighting agent, 100 grams of LATEX 2000TM latex (with the exception of Batch 8), and components in the amounts listed in **TABLE 2** (including a C₁₅ alcohol ethoxylated with 15 moles of ethylene oxide, which is available from Halliburton Energy Services of Duncan, under the trademark "434BTM") were added to form eight batches. Each of the batches was mixed in a Waring blender. The batches were poured into receptacles and incubated at the temperatures listed.

TABLE 2

Component	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8 (500 g latex)
FLEXCEM COMPONENT L TM dithio carbamate	5.6g	5.6g	0.75g	0.75g	4.5g	4.5g	1.5g	2g
Zinc Oxide	9g	9g	14g	14g	22.5g	22.5g	14g	15g
Sulfur	9g	9g	9g	9g	13.5g	13.5g	9g	10g
Stearic acid	--	--	4.5g	--	--	--	--	--
D-AIR3 TM acetylenic alcohol	14.6g	14.6g	3g	3g	3g	3g	--	5g
MICROMAX TM manganese oxide (15.3lb/gal)	600g	600g	400g	400g	400g	400g	400g	400g

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Component	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8 (500 g latex)
434B TM ethoxylated alcohol	- -	45g	45g	45g	45g	45g	26g	10g
Comments	Latex inverted	No set; 48hr at 80°F	No set; 24hr at 140°F	No set; 24hr at 140°F	Set; 48hr at 140°F	No set; 48hr at 200°F	No set; 24hr at 200°F	No set; 72hr at 200°F

TABLE 2 shows that the fifth batch set without stearic acid.

EXAMPLE 3

To test curing properties of the second embodiment, LATEX 2000TM latex in the amounts listed in TABLES 3A and 3B, were mixed with components in the amounts listed in TABLES 3A and 3B (including a C₁₅ alcohol ethoxylated with 40 moles of ethylene oxide, which is available from Halliburton Energy Services of Duncan, under the trademark "434CTM," a sodium salt of alpha-olefinic sulfonic acid surfactant which is discussed in U.S. Patent No. 5,588,489, the entire disclosure of which is incorporated herein as if reproduced in its entirety, and is available from Halliburton Energy Services of Duncan, under the trademark "AQF-2TM," an alcohol ether sulfate surfactant which is discussed in U.S. Patent No. 5,588,489, the entire disclosure of which is incorporated herein as if reproduced in its entirety, and is available from Halliburton Energy Services of Duncan, under the trademark "HOWCO SUDSTM," and ammonium decasulfate, which is available from Halliburton Energy Services of Duncan, under the trademark "CFASTM") were added to form twelve batches. Each of the batches was mixed in a Waring blender with a sealable metal canister. The batches were poured into receptacles and incubated at the

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temperatures listed.

TABLE 3A

Components	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7
LATEX 2000 TM latex	450g	450g	450g	450g	450g	600g	600g
FLEXCEM COMPONEN T L TM dithio carbamate	5.6g	5.6g	5.6g	5.6g	5.6g	6g	6g
Zinc Oxide	9g	9g	9g	9g	9g	30g	30g
Sulfur	9g	9g	9g	9g	9g	18g	18g
Stearic acid	9g	9g	9g	9g	9g	--	--
D-AIR3 TM acetylenic alcohol	14.6g	14.6g	--	--	--	--	--
SSA-1 TM silica flour	600g	600g	--	--	--	--	--
ZONE SEAL 2000 TM surfactant	9g	18g	--	20g	20g	--	--
MICROSAND TM crystalline silica	--	--	600g	600g	600g	--	--
434C TM ethoxylated alcohol	--	--	45g	45g	45g	--	--
AQF-2 TM surfactant	--	--	9g	--	--	--	--

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Components	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7
HC-2 TM surfactant	--	--	4.5g	--	--	10g	5g
HOWCO SUDS TM surfactant	--	--	--	--	--	--	10g
CFAS TM ammonium decasulfate	--	--	--	--	--	--	--
Comments	Unstable foam	Unstable foam	Unstable foam	Unstable foam	Unstable foam	Unstable foam	Unstable foam

TABLE 3B

Components	Batch 8	Batch 9	Batch 10	Batch 11	Batch 12
LATEX 2000 TM latex	600g	600g	600g	600g	675g
FLEXCEM COMPONENT L TM dithio carbamate	6g	6g	6g	6g	8.4g
Zinc Oxide	30g	30g	30g	30g	13.5g
Sulfur	18g	18g	18g	18g	13.5g
Stearic acid	--	--	--	--	13.5g
D-AIR3 TM acetylenic alcohol	--	--	--	--	--
SSA-1 TM silica flour	--	--	--	--	--

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Components	Batch 8	Batch 9	Batch 10	Batch 11	Batch 12
ZONE SEAL 2000 TM surfactant	--	--	--	--	20g
MICROSAND TM M crystalline silica	--	--	200g	200g	600g
434C TM ethoxylated alcohol	--	--	--	--	--
AQF-2 TM surfactant	10g	--	--	--	--
HC-2 TM surfactant	5g	5g	12g	20g	--
HOWCO SUDS TM surfactant	--	--	--	--	--
CFAS TM ammonium decasulfate	--	10g	--	--	--
Comments	Unstable foam	Unstable foam	Unstable foam	Foamed and placed in cell for 48 hours at 150°F; set stable foam	Foamed and placed in cell; heated to 190°F for 2 hours; sand settled from top 1-2 inches of 8 inch column

TABLES 3A and 3B show that the eleventh and twelfth batches set.

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EXAMPLE 4

To test curing properties of the first embodiment, 300 grams of LATEX 2000TM latex, 2 grams D-AIR3TM acetylenic alcohol, and components in the amounts listed in **TABLE 4** were added to form eight batches. Each of the batches was mixed in a Waring blender. The batches were poured into receptacles and incubated in a 150°F water bath.

TABLE 4

Component	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8
FLEXCEM COMPONEN T L TM dithio carbamate	3g	3g	3g	--	--	--	--	3g
Zinc Oxide	--	15g	15g	15g	15g	--	--	--
Sulfur	9g	--	9g	9g	--	9g	--	--
Stearic acid	3g	3g	--	3g	--	--	3g	--
Comments	No set	No set	Set	No set	No set	No set	No set	No set

TABLE 4 shows that the fourth batch set.

EXAMPLE 5

To test shear bond properties of the first embodiment, 450 grams of LATEX 2000TM latex, 1.5 grams of FLEXCEM COMPONENT LTM dithio carbamate, 2 grams of D-AIR3TM acetylenic alcohol, and components in the amounts listed in **TABLE 5** were added to form eight batches. Each of the batches was mixed in a Waring blender. The batches were poured into receptacles and incubated before having their shear bond strengths tested. Batches 1-4 were tested after incubation for 48 hours at 200°F. Batches 5-8 were tested after incubation for 12 days at 200°F.

In a conventional shear bond test, the batches were placed in metal cylinders

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with a metal bar disposed in each of the cylinders. Once a batch set, the bar was supported and positioned by the composition. Shear bond strength was determined by the force required to push the bar out of the cylinder. The shear bond testing method is conventional, and is described in a paper by L. G. Carter and G. W. Evans entitled "A Study of Cement-Pipe Bonding," presented at the Society of Petroleum Engineers California Regional Meeting, held in Santa Barbara, CA, on Oct 24-25, 1963.

TABLE 5

Component	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8
Zinc Oxide	13.5g	13.5g	27g	27g	13.5g	13.5g	13.5g	13.5g
Sulfur	9g	18g	9g	18g	9g	9g	9g	9g
SSA-1 TM silica flour	600g	600g	600g	600g	--	200g	400g	600g
Shear bond	21 psi	14 psi	26 psi	22 psi	11 psi	28 psi	34 psi	34 psi

TABLE 5 shows that all the batches bond to metal. Batch 1 also shear bond strengths of 40 psi at 72 hours, 38 psi at 96 hours, and 55 psi at 30 days.

EXAMPLE 6

To test thickening times (TT) for reaching viscosities of 70 BC for the first embodiment, 600 grams of LATEX 2000TM latex, 3 grams of D-AIR3TM acetylenic alcohol, and components listed in the amounts listed in **TABLE 6** were added to form ten batches. Each of the batches was mixed in a Waring blender. The batches were poured into receptacles and incubated at the temperatures listed in **TABLE 6**.

TABLE 6

Component	Bat. 1	Bat. 2	Bat. 3	Bat. 4	Bat. 5	Bat. 6	Bat. 7	Bat. 8	Bat. 9	Bat. 10
FLEXCEM COMPONEN T L™ dithio carbamate	6g	0.75g	0.75g	1.1g	0.75g	1g	1g	2g	--	--
Zinc Oxide	30g	3g	6g	12g	18g	18g	18g	18g	18g	18g
Sulfur	18g	12g	12g	12g	12g	12g	12g	12g	12g	12g
Stearic acid	6g	6g	6g	6g	6g	12g	--	--	12g	--
TT (hr:min) at 150°F	1:39; 1:53	12+	10:26	8:20	7:37	7:44	6:00	3:39	--	--
TT (hr:min) at 200°F	--	--	--	--	--	1:59	1:45	1:35	6:42	11+

TABLE 6 shows that the set up times can be controlled by varying the amounts of components.

EXAMPLE 7

To test applied pressure for the first and second embodiments, LATEX 2000™ latex, and components listed in the amounts listed in **TABLE 7** were added to form three batches. Each of the batches was mixed in a Waring blender.

The first batch, representing the first embodiment, was poured into a test cell, which was sealed and heated to 200°F for 72 hours. After 72 hours, a valve positioned under a 325 mesh screen on the bottom of the test cell was opened, and a force of 1000 psi was applied to the test cell via a piston from the top of the cell. After approximately an hour, the volume of the batch had reduced by an amount listed in **TABLE 7**.

The second batch, representing the second embodiment, was poured into a test cell, which was sealed and heated to 170°F. After 48 hours, a force of 1000 psi was

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applied to the test cell via a piston, and the volume of the batch had reduced by an amount listed in **TABLE 7**. After seven days, pressure was released, and the volume of the batch returned to 85% of its original size.

The third batch, representing the second embodiment, was poured into a test cell, heated to 170°F, and thereafter, a force of 1000 psi was applied to the test cell via a piston. The volume of the batch was reduced by an amount listed in **TABLE 7**. After twenty four hours, pressure was released, and the volume of the batch returned to its original size. Thereafter, a force of 1000 psi was applied again and the volume of the batch was reduced by an amount listed in **TABLE 7**. After twenty four hours, pressure was again released, and the volume of the batch returned to 88% of its original size.

TABLE 7

Component	Batch 1 Non-foamed Latex	Batch 2 Set Foamed Latex	Batch 3 Liquid Foam Latex
LATEX 2000 TM latex	450g	600g	600g
FLEXCEM COMPONENT L TM dithio carbamate	1.5g	6g	6g
Zinc Oxide	13.5g	30g	30
Sulfur	9g	18g	6g
HC-2 TM surfactant	- -	20g	20g
SSA-1 TM silica flour	400g	- -	- -
Volume reduction	30%	40%	36%

TABLE 7 shows that the first embodiment is compressible in its set state when placed against a porous geological formation, and the second embodiment is compressible in both set and unset states when placed in a sealed system.

The methods of the present invention for sealing an expandable tubular such as

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a pipe, pipe string, casing, liner or the like in a wellbore in a subterranean formation basically comprise placing the expandable tubular in the wellbore, placing a sealing composition as described herein into the wellbore, expanding the expandable tubular, and allowing the sealing composition to set in the wellbore. The methods may optionally comprise the step of foaming the sealant composition using a gas such as nitrogen or air. In performing the described methods, the step of placing the expandable tubular in the wellbore may be performed before or after the step of placing the sealing composition into the wellbore. The step of expanding the expandable tubular may also be performed before or after the step of placing the sealing composition into the wellbore. Furthermore, the expandable tubular may be expanded before, after or during the set of the sealing composition. Where the tubular is expanded during or after the set of the sealing composition, preferred resilient compositions of the present invention will remain competent due to their elasticity and compressibility.

In addition to the foregoing methods, the wellbore may extend or be additionally extended into the subterranean formation below the first tubular wherein a second tubular, such as a pipe, pipe string, casing, liner or the like, is placed in the wellbore below the first tubular such that a portion of the second tubular extends into the first tubular. A second sealing composition, in accordance to the embodiments described herein, is placed in the wellbore located below the first tubular and the second tubular is expanded in the wellbore. The step of placing the second tubular in the wellbore may be performed before or after the step of placing the second sealing composition into the wellbore and the step of expanding the second tubular may also be performed before or after the step of placing the second sealing composition into the wellbore. The second tubular may also be expanded before, after or during the set of the either sealing composition. Furthermore, although the first and second tubulars may be expanded at the same time, when the second tubular is expanded inside the previously expanded first tubular, the second tubular may provide additional expansion to an overlapping portion of the first tubular whereby the sealing

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composition located behind that overlapping portion of the first tubular is further compressed thereby but remains competent due to its elasticity and compressibility.

Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many other modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention as defined in the following claims.

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CLAIMS:

1. A method of sealing an expandable tubular in a wellbore comprising the steps of:
 - placing the expandable tubular in the wellbore;
 - placing a resilient sealing composition into the wellbore;
 - expanding the expandable tubular; and
 - allowing the sealing composition to set in the wellbore.
2. The method of claim 1 wherein the sealing composition comprises a polymer and a metal containing compound.
3. The method of claim 2 wherein the sealing composition comprises a copolymer, terpolymer, or interpolymer.
4. The method of claim 2 wherein the polymer comprises a latex and the sealing composition further comprises sulfur.
5. The method of claim 4 wherein the latex comprises a styrene/butadiene copolymer.
6. The method of claim 4 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion.
7. The method of claim 4 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.
8. The method of claim 4 wherein the latex is selected from the group consisting

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of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

9. The method of claim 8 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

10. The method of claim 2 wherein the polymer comprises an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer.

11. The method of claim 10 wherein the halogenated derivatives are halogenated with chlorine or bromine.

12. The method of claim 2 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

13. The method of claim 12 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

14. The method of claim 1 wherein the sealing composition comprises latex, dithio carbamate, metal containing compound, and sulfur.

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15. The method of claim 14 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.
16. The method of claim 15 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.
17. The method of claim 14 wherein the metal containing compound is zinc oxide.
18. The method of claim 14 wherein the latex is a styrene/butadiene copolymer latex emulsion.
19. The method of claim 14 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion.
20. The method of claim 14 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.
21. The method of claim 14 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.
22. The method of claim 21 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.
23. The method of claim 14 wherein the dithio carbamate is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.

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24. The method of claim 14 wherein the metal containing compound is present in a range of 2% to 5% by weight of the latex in the sealing composition.
25. The method of claim 14 wherein the sulfur is present in a range of 1 % to 4% by weight of the latex in the sealing composition.
26. The method of claim 14 wherein the sealing composition further comprises stearic acid.
27. The method of claim 26 wherein the stearic acid is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.
28. The method of claim 14 wherein the sealing composition further comprises a weighting agent.
29. The method of claim 28 wherein the weighting agent is present in a range of 0.1% to 150% by weight of the latex in the sealing composition.
30. The method of claim 14 wherein the sealing composition further comprises acetylenic alcohol.
31. The method of claim 14 wherein the acetylenic alcohol is present in a range of 0.001% to 0.2% by weight of the latex in the sealing composition.
32. The method of claim 14 wherein the sealing composition further comprises a foaming agent.
33. The method of claim 17 wherein the foaming agent is present in a range of 2% to 4% by weight of the latex in the sealing composition.

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34. The method of claim 1 wherein the expandable tubular is expanded during or after the set of the sealing composition.
35. The method of claim 1 wherein the sealant composition is foamed with a gas.
36. The method of claim 35 wherein the sealant composition is foamed using nitrogen or air.
37. The method of claim 35 wherein the gas is generally present in the range of from about 0% to about 40% by volume of the sealing composition.
38. A method of sealing an expandable tubular in a wellbore comprising the steps of:
- placing the expandable tubular in the wellbore;
 - placing a polymeric sealing composition into the wellbore;
 - expanding the expandable tubular; and
 - allowing the sealing composition to set in the wellbore.
39. The method of claim 38 wherein the polymeric sealing composition comprises a copolymer, terpolymer, or interpolymer.
40. The method of claim 38 wherein the sealing composition comprises latex and sulfur.
41. The method of claim 40 wherein the latex comprises a styrene/butadiene copolymer.
42. The method of claim 40 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight

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aqueous emulsion.

43. The method of claim 40 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.

44. The method of claim 40 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

45. The method of claim 44 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

46. The method of claim 38 wherein the sealing composition comprises an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer.

47. The method of claim 46 wherein the halogenated derivatives are halogenated with chlorine or bromine.

48. The method of claim 38 wherein the sealing composition comprises a metal containing compound.

49. The method of claim 48 wherein the metal containing compound comprises

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zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

50. The method of claim 49 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

51. The method of claim 38 wherein the sealing composition comprises latex, dithio carbamate, metal containing compound, and sulfur.

52. The method of claim 51 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

53. The method of claim 51 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

54. The method of claim 51 wherein the metal containing compound is zinc oxide.

55. The method of claim 51 wherein the latex is a styrene/butadiene copolymer latex emulsion.

56. The method of claim 51 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion.

57. The method of claim 51 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.

58. The method of claim 51 wherein the latex is selected from the group consisting

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of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

59. The method of claim 58 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

60. The method of claim 51 wherein the dithio carbamate is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.

61. The method of claim 51 wherein the metal containing compound is present in a range of 2% to 5% by weight of the latex in the sealing composition.

62. The method of claim 51 wherein the sulfur is present in a range of 1 % to 4% by weight of the latex in the sealing composition.

63. The method of claim 51 wherein the sealing composition further comprises stearic acid.

64. The method of claim 63 wherein the stearic acid is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.

65. The method of claim 51 wherein the sealing composition further comprises a weighting agent.

66. The method of claim 65 wherein the weighting agent is present in a range of 0.1% to 150% by weight of the latex in the sealing composition.

67. The method of claim 51 wherein the sealing composition further comprises

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acetylenic alcohol.

68. The method of claim 51 wherein the acetylenic alcohol is present in a range of 0.001% to 0.2% by weight of the latex in the sealing composition.

69. The method of claim 51 wherein the sealing composition further comprises a foaming agent.

70. The method of claim 69 wherein the foaming agent is present in a range of 2% to 4% by weight of the latex in the sealing composition.

71. The method of claim 38 wherein the expandable tubular is expanded during or after the set of the sealing composition.

72. The method of claim 38 wherein the sealant composition is foamed with a gas.

73. The method of claim 72 wherein the sealant composition is foamed using nitrogen or air.

74. The method of claim 72 wherein the gas is generally present in the range of from about 0% to about 40% by volume of the sealing composition.

75. A method of sealing an expandable tubular in a wellbore comprising the steps of:

- placing the expandable tubular in the wellbore;
- placing a foamed sealing composition into the wellbore;
- expanding the expandable tubular; and
- allowing the sealing composition to set in the wellbore.

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76. The method of claim 75 wherein the sealing composition comprises a foaming agent.
77. The method of claim 75 wherein the sealing composition comprises a gas.
78. The method of claim 75 wherein the gas is selected from the group consisting of nitrogen and air.
79. The method of claim 75 wherein the gas is generally present in the range of from about 0% to about 40% by volume of the sealing composition.
80. The method of claim 75 wherein the sealing composition comprises a polymer and a metal containing compound.
81. The method of claim 80 wherein the sealing composition comprises a copolymer, terpolymer, or interpolymer.
82. The method of claim 80 wherein the polymer comprises a latex and the sealing composition further comprises sulfur.
83. The method of claim 82 wherein the latex comprises a styrene/butadiene copolymer.
84. The method of claim 82 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion.
85. The method of claim 82 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.

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86. The method of claim 82 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

87. The method of claim 86 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

88. The method of claim 80 wherein the polymer comprises an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer.

89. The method of claim 88 wherein the halogenated derivatives are halogenated with chlorine or bromine.

90. The method of claim 80 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

91. The method of claim 90 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

92. The method of claim 75 wherein the sealing composition comprises latex, dithio carbamate, metal containing compound, and sulfur.

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93. The method of claim 92 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

94. The method of claim 93 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

95. The method of claim 92 wherein the metal containing compound is zinc oxide.

96. The method of claim 92 wherein the latex is a styrene/butadiene copolymer latex emulsion.

97. The method of claim 92 wherein the latex has a styrene/butadiene weight ratio of about 25:75, with the styrene/butadiene copolymer suspended in a 50% by weight aqueous emulsion.

98. The method of claim 92 wherein the latex is present in a range of 41% to 90% by weight of the sealing composition.

99. The method of claim 92 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

100. The method of claim 99 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

101. The method of claim 92 wherein the dithio carbamate is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.

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102. The method of claim 92 wherein the metal containing compound is present in a range of 2% to 5% by weight of the latex in the sealing composition.

103. The method of claim 92 wherein the sulfur is present in a range of 1 % to 4% by weight of the latex in the sealing composition.

104. The method of claim 92 wherein the sealing composition further comprises stearic acid.

105. The method of claim 104 wherein the stearic acid is present in a range of 0.1% to 2% by weight of the latex in the sealing composition.

106. The method of claim 92 wherein the sealing composition further comprises a weighting agent.

107. The method of claim 106 wherein the weighting agent is present in a range of 0.1% to 150% by weight of the latex in the sealing composition.

108. The method of claim 92 wherein the sealing composition further comprises acetylenic alcohol.

109. The method of claim 92 wherein the acetylenic alcohol is present in a range of 0.001% to 0.2% by weight of the latex in the sealing composition.

110. The method of claim 92 wherein the sealing composition further comprises a foaming agent.

111. The method of claim 110 wherein the foaming agent is present in a range of 2% to 4% by weight of the latex in the sealing composition.

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112. The method of claim 75 wherein the expandable tubular is expanded during or after the set of the sealing composition.

113. A method of sealing an expandable tubular in a wellbore comprising the steps of:

- (a) placing the expandable tubular in the wellbore;
- (b) placing a resilient sealing composition into the wellbore before or after step (a);
- (c) expanding the expandable tubular before or after step (b); and
- (d) allowing the sealing composition to set in the wellbore before, after or during step (c).

114. The method of claim 113 wherein the sealing composition comprises a polymer selected from the group consisting of a copolymer, terpolymer, or interpolymer.

115. The method of claim 114 wherein the polymer comprises a latex and the sealing composition further comprises sulfur.

116. The method of claim 115 wherein the latex comprises a styrene/butadiene copolymer.

117. The method of claim 114 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

118. The method of claim 117 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber, acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

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119. The method of claim 113 wherein the sealing composition comprises a polymer selected from the group consisting of an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer.

120. The method of claim 113 wherein the sealing composition comprises latex, dithio carbamate, metal containing compound, and sulfur.

121. The method of claim 120 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

122. The method of claim 121 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

123. The method of claim 113 wherein the sealing composition is foamed with a gas.

124. The method of claim 123 wherein the gas is generally present in the range of from about 0% to about 40% by volume of the sealing composition.

125. A method of sealing expandable tubulars in a wellbore comprising the steps of:

- (a) placing a first expandable tubular in the wellbore;
- (b) placing a first resilient sealing composition into the wellbore before or

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- after step (a);
- (c) expanding the first expandable tubular before or after step (b);
 - (d) allowing the first resilient sealing composition to set in the wellbore before, after or during step (c);
 - (e) having or extending the wellbore extend below the first expandable tubular;
 - (f) placing a second expandable tubular in the wellbore;
 - (g) placing a second resilient sealing composition into the wellbore before or after step (f);
 - (h) expanding the second expandable tubular before or after step (g); and
 - (i) allowing the second resilient sealing composition to set in the wellbore before, after or during step (h).

126. The method of claim 125 wherein at least one of said first and second sealing compositions comprises a polymer selected from the group consisting of a copolymer, terpolymer, or interpolymer.

127. The method of claim 125 wherein at least one of said first and second sealing compositions comprises latex and sulfur.

128. The method of claim 127 wherein the latex comprises a styrene/butadiene copolymer.

129. The method of claim 127 wherein the latex is selected from the group consisting of natural rubber, modified natural rubber, synthetic polymers and blends thereof.

130. The method of claim 129 wherein the synthetic polymers are selected from the group consisting of styrene/butadiene rubber, polybutadiene rubber, neoprene rubber,

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acrylonitrile/butadiene rubber, polyisoprene rubber, isobutylene/isoprene rubber, and ethylene/propylene rubber.

131. The method of claim 125 wherein at least one of said first and second sealing compositions comprises a polymer selected from the group consisting of an ethylene propylene diene polymer, an isobutylene-isoprene copolymer, halogenated derivatives of an isobutylene-isoprene copolymer, a butadiene-isoprene copolymer, a poly(isobutylene-co-styrene) polymer, halogenated derivatives of a poly(isobutylene-co-styrene) polymer, a poly(isobutylene-co-alkyl styrene) polymer, halogenated derivatives of a poly(isobutylene-co-alkyl styrene) polymer, a poly(isobutylene-co-haloalkyl styrene) polymer and halogenated derivatives of a poly(isobutylene-co-haloalkyl styrene) polymer.

132. The method of claim 125 wherein at least one of said first and second sealing compositions comprises latex, dithio carbamate, metal containing compound, and sulfur.

133. The method of claim 132 wherein the metal containing compound comprises zinc, tin, iron, selenium, magnesium, chromium, nickel, or cadmium.

134. The method of claim 133 wherein the metal containing compound comprises an oxide, a carboxylic acid salt, a complex with a dithiocarbamate ligand, or a complex with a mercaptobenzothiazole ligand.

135. The method of claim 125 at least one of said first and second sealing compositions is foamed with a gas.

136. The method of claim 135 wherein the gas is generally present in the range of from about 0% to about 40% by volume of the sealing composition.

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137. The method of claim 135 further comprising the steps of:
- (i) extending the second tubular into the first tubular after the first tubular has been expanded and the first sealing composition is placed in the wellbore;
 - (j) expanding the second tubular in the first tubular; and
 - (k) providing additional expansion to said first tubular wherein the first sealing composition is further compressed but remains competent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/05416

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 E21B33/138 E21B33/14 E21B33/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 520 839 A (HALLIBURTON CO) 30 December 1992 (1992-12-30)	1-10, 12, 14, 15, 17-29, 32-46, 48, 49, 51, 52, 54-66, 69-88, 90, 92, 93, 95-107, 110-121, 123, 124
Y	column 2, line 28 - column 3, line 11 column 4, line 49 column 5, line 15 - column 7, line 20 column 8, line 20 - line 31 column 9, line 1 - line 27 --- -/--	125-137

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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